

Features of water vapor sorption by cellulose materials

Michael Jacob Ioelovich *

Designer Energy, Chemical Department, Rehovot 7670504, Israel.

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Abstract

In this research, the sorption of water vapor (WV) by various cellulose samples (microcrystalline cellulose, cotton cellulose, Kraft pulp, mercerized cellulose, and rayon fibers) has been studied. The sorption isotherms of WV for various samples have a sigmoid shape. To describe such isotherms, various models have been proposed, including mono- and multimolecular adsorption, formation of hydrates and solid solutions, as well as mixed models combining various sorption mechanisms. After critical analysis of known models, the improved absorption model was proposed to explain the interaction of WV with cellulose samples. It was confirmed that crystallites are inaccessible for water, and therefore water molecules can be trapped only by polar groups of non-crystalline (amorphous) domains of cellulose materials. The developed model permitted obtaining the general absorption isotherm of water molecules in amorphous domains of cellulose. Moreover, the equation was derived, which describes both the general isotherm and isotherm of any semi-crystalline cellulose sample, when its crystallinity or amorphicity degree was pre-determined. Based on the proposed absorption model, various characteristics can be found, e.g., degrees of amorphicity and crystallinity, the maximum amount of absorbed water, the specific surface area of wet cellulose sample, the amount of capillary condensed water, etc.

Keywords: Sorption of Water Vapor; Cellulose; Amorphous Domains; Structure; Specific Surface Area; Calculations

1. Introduction

Water is a constant companion of cellulosic materials that accompanies this hydrophilic biopolymer in nature and during the production, use, and storage of various cellulosic materials. Therefore, the sorption of water vapor (WV) by cellulose has been studied for many years, and numerous monographs, reviews, and research articles have been devoted to this issue [1-7].

Despite intensive research, the sorption mechanism has not been fully disclosed. When studying the sorption isotherms of water vapor for cellulose materials it was found that these isotherms have a sigmoid shape, i.e., they are type II [4]. To describe these sorption isotherms, various models were proposed according to which the sorption of water vapor by cellulose was explained by mono- and multimolecular adsorption [8], formation of hydrates and solid solutions [2, 4, 9, 10], and by mixed models combining various mechanisms such as surface adsorption, dissolution, clustering of water molecules, etc. [11-13].

Hailwood and Horrobin's model considered the interaction of WV with cellulose as a dissolution process with the formation of monohydrates at the initial sorption stage, and then polyhydrates [2, 4]. Park discussed a more complex model, which combined the Langmuir equation of monolayer surface adsorption at the initial stage, Henry's equation of water vapor absorption at the middle stage, and a power-law equation describing the clustering of water molecules at the last stage of sorption [12, 13].

* Corresponding author: Michael Ioelovich
Designer Energy, Chemical Department, Rehovot 7670504, Israel.

There are also other models of WV sorption by cellulose materials, which, however, are not widely used [2, 8, 14]. For example, according to the proposed hypothesis [14], the sorption of WV by a rigid sorbent such as cellulose causes its cracking and splitting into microfibrils, which leads to a sharp increase in the specific surface area and adsorption capacity of the initially non-porous polymer.

The purpose of this study was to analyze various sorption models and substantiate the most realistic sorption mechanism of water vapor by cellulose materials.

2. Material and methods

2.1. Materials

The following cellulose samples were investigated:

- Microcrystalline cellulose (MC) Avicel PH-301 of FMC BioPolymer Co.
- Pure chemical-grade cotton cellulose (CC) of Hercules Co.
- Bleached spruce Kraft pulp (KP) of Weyerhaeuser Co.
- Mercerized Kraft pulp (MP) prepared by treatment KP with 20% NaOH and following washing and drying.
- Rayon fibers (RF) of Rayonier Inc.

2.2. Sorption of vapors

The sorption experiments were carried out at 298 K on a *vacuum Mac-Ben apparatus* having helical spring quartz scales. Sorbates were water and n-hexane. Before starting the experiments, the samples were dried at 383 K up to constant weight and additionally degassed under vacuum in the sorption device. Three of the same samples were tested to calculate an average sorption value and standard deviation that was in the range ± 0.002 g/g. The specific surface area (S_{sp}) of the samples was measured from isotherms by the BET method. Using this method, the value of s_o (g/g) corresponding to the inflection point of the initial stage of isotherms was found, after which the value of S_{sp} was calculated, as follows.

In the case of n-hexane vapor

$$S_{sp} \left(\frac{m^2}{g} \right) = 2087 s_o \dots \dots \dots (1)$$

In the case of water vapor

$$S_{sp} (m^2/g) = 3516 s_o \dots \dots \dots (2)$$

2.3. Enthalpy of Wetting

The wetting enthalpies of cellulose samples (ΔH) were studied at 298 K by the method of precise microcalorimetry using a TAM III calorimeter [15, 16]. The samples were preliminarily dried at 383 K in a vacuum chamber to constant weight. Three of the same samples were tested to calculate an average enthalpy value and standard deviation that was in the range ± 0.02 J/g. Using calorimetric measurements, the crystallinity (X) and amorphicity (Y) degrees of the samples were determined [15]:

$$X = 1 - (\Delta H/\Delta H_a) \dots \dots \dots (3)$$

$$Y = \Delta H/\Delta H_a \dots \dots \dots (4)$$

Where $\Delta H_a = -168$ (J/g) is the enthalpy of wetting for completely amorphous cellulose.

3. Results and discussion

Sorption isotherms of n-hexane vapor for dry cellulose samples resemble isotherms of I (b) type, which have an initial steep part and then a gentle plateau (Figure 1). Despite higher crystallinity ($X=0.75$), the sample of microcrystalline

cellulose (MC) has a higher sorption value than the less crystalline sample of rayon fibers (RF) ($X=0.36$). As a result, fine MC powder exhibits a higher specific surface area, $S_{sp}(H)$ (Table 1). Nevertheless, in all cases, the sorption value of n-hexane for cellulose samples was relatively small, several milligrams per gram of dry sorbent. These features indicate the adsorption mechanism of the inert sorbate molecules on the surface of a low-porous biopolymer.

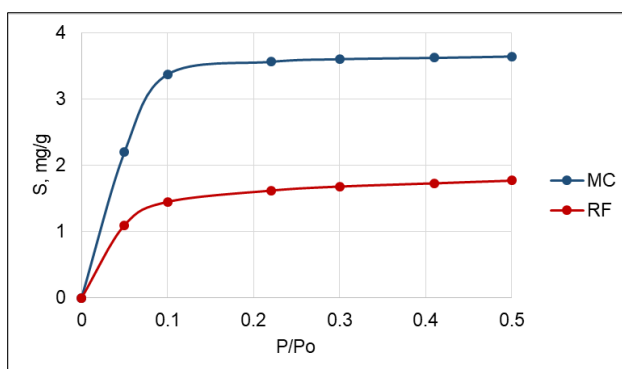


Figure 1 Sorption isotherms of n-hexane vapor for samples of microcrystalline cellulose (MC) and rayon fibers (RF)

Table 1 Structural characteristics of cellulose samples*

Sample	$-\Delta H, J/g$	X	Y	$S_{sp}(H), m^2/g$	$S_{sp}(W), m^2/g$
MC	42	0.75	0.25	7.1	85
CC	51	0.70	0.30	5.4	110
KP	61	0.64	0.36	6.3	120
MP	79	0.53	0.47	3.7	160
RF	108	0.36	0.64	3.0	220

* $S_{sp}(H), S_{sp}(W)$ denote specific surface area measured by sorption of n-hexane vapor, and water vapor, respectively

In contrast to isotherms of type 1(b) characteristic for surface adsorption of inert sorbates (e.g., n-hexane), the sorption isotherms of water vapor (WV) for various cellulose materials had sigmoid shapes, and therefore they can be classified as type II (see e.g., Figure 2).

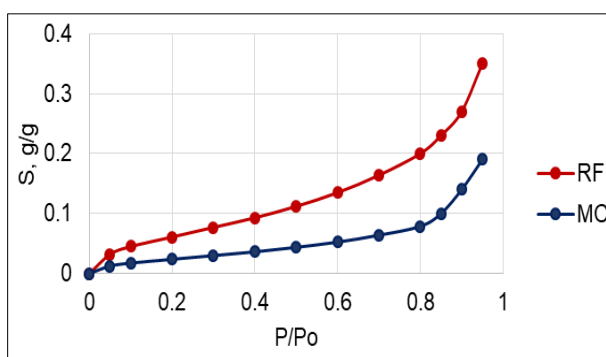


Figure 2 Sorption isotherms of water vapor for samples of microcrystalline cellulose, MC ($Y=0.25$), and rayon fibers, RF ($Y=0.64$)

Isotherms of this type have an initial steep stage, after which a gradual and then an accelerated increase in sorption is observed, and finally, at high relative vapor pressures, a sharp rise in the sorption of WV occurs.

In the coordinates of the BET equation, $Z = \varphi / [S(1-\varphi)] = F(\varphi)$, where $\varphi = P/Po$, the sorption isotherms of WV are generally nonlinear (Figure 3). In addition, the sorption value of water vapor by cellulose samples does not correlate

with the specific surface area measured by the sorption of inert vapor. Moreover, the higher the degree of amorphicity (Y) of the sample, the greater the sorption of WV (Figure 2).

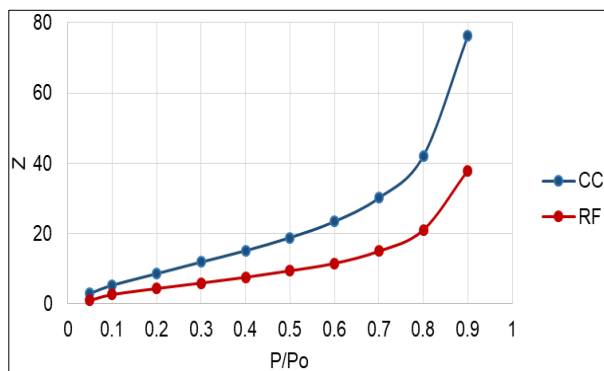


Figure 3 Sorption isotherms of water vapor by cotton cellulose (CC) and rayon fibers (RF) in coordinates of BET - equation

If using a linear section of BET isotherms in the φ range from 0.1 to 0.5, then it is possible to find the s_o -value and estimate the specific surface of the samples, measured by WV sorption. The obtained specific surface area of wet cellulose samples, $S_{sp}(W)$, is very high and reaches several hundred square meters per gram although all studied samples in the dry state were low-porous (Table 1). Moreover, the study showed, there is no clear correlation between $S_{sp}(W)$ and $S_{sp}(H)$. On the other hand, the linear correlation between the $S_{sp}(W)$ value and the degree of amorphicity (Y) of samples is observed (Figure 4), which evidences the absorption mechanism sorption of WV in amorphous domains of various celluloses.

The application of the GAB equation of multimolecular adsorption is also difficult [17]. The common three-parameter GAB equation describes the sorption isotherms with low accuracy, especially at increased relative vapor pressures or water vapor activities. If the number of parameters is increased, the accuracy improves. However, in this case, the parameter of monolayer capacity changes, and the calculations of the specific surface area of the biopolymer become unreliable.

Thus, the sorption of water vapor by cellulose cannot be explained through the models of multimolecular surface adsorption. The $S_{sp}(W)$ value does not characterize the real porous structure of cellulose. Moreover, the $S_{sp}(W)$ can be considered as an index of the accessibility of the internal structure of this biopolymer to water vapor, which depends on the degree of amorphicity.

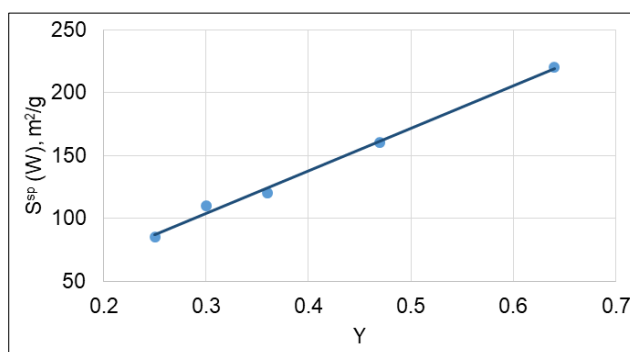


Figure 4 Dependence of specific surface area, $S_{sp}(W)$, on amorphicity degree, Y , of samples

The hypothesis of micro-cracking of rigid cellulose under the action of water vapor as a cause of an increase in sorption value [14] is of interest, but not experimentally confirmed. This hypothesis cannot explain why a sample with low crystallinity and therefore low rigidity (e.g., RF), has an increased sorption value than a high-crystalline and rigid cellulose sample (e.g., MC), although the cracking ability of a low-rigid sample should be less. If cellulose cracks and splits into microfibrils under the action of WV, then how is it possible to keep paper sheets intact when printed in a humid atmosphere? In addition, how can make fabrics on looms in a humid atmosphere if the cellulose fibers are

cracked? Based on such a hypothesis, it is also difficult to explain such a well-known fact as an increase in the tensile strength of natural cellulose fibers after the sorption of WV [18-20].

Hailwood and Horrobin postulated the dissolution of VW in the internal structure of cellulose during the sorption process with the formation of monohydrates and polyhydrates [2, 4]. However, this hypothesis is doubtful since cellulose cannot form chemical compounds with water such as monohydrates. It has also not been proven that the formation of polyhydrates should lead to a hyperbolic increase in the amount of sorbed water. The parameters of Hailwood and Horrobin's equation are selected in such a way as to achieve the best agreement with the experimental isotherm. This assists to adapt the model to the experiment but does not provide arguments about the real sorption mechanism.

According to Park's model, the sorption of water vapor by a hydrophilic polymer such as cellulose is a complex process combining monomolecular adsorption at the initial stage, dissolution of water vapor in the biopolymer at the middle stage, and clustering, i.e., multimolecular sorption, at the last stage [12]. However, as shown above (Table 1), in reality, the dry cellulose materials are low-porous and therefore can adsorb the negligible amount of water vapor on the surface of micro- and mesopores at the initial stage. On the other hand, the linear dissolution process of water vapor in the biopolymer following Henry's law is also unlikely, since this law is observed only for ideal solutions, to which the cellulose-water system does not belong. Nobody detected the clustering of water molecules in cellulose at the last sorption stage. Instead, such phenomena were noted as the transition of wet amorphous domains of cellulose to a viscoelastic state, as well as capillary condensation of WV in mesopores [2, 21-23].

In addition, to describe each isotherm, Park's model requires the determination of at least five parameters [13]. If it is necessary to describe the isotherm of WV for another sample, then the new five parameters must be recalculated. Thus, Park's model is mathematically adapted to the experimental isotherm without proof of the sorption mechanism.

Due to the insufficient validity of the known models, additional studies are required to develop an improved sorption model. As was shown for two cellulose samples, their sorption isotherms have a characteristic sigmoid shape (Figure 2). Other cellulose samples have a similar shape (Figure 5).

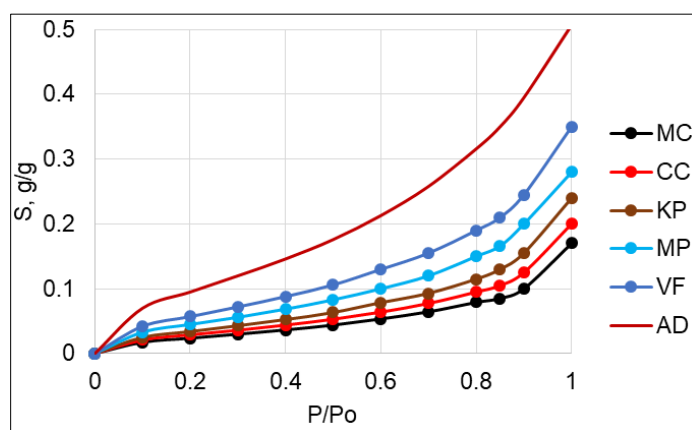


Figure 5 Sorption isotherms of water vapor for various cellulose samples and their amorphous domains (AD)

The analysis of these isotherms showed the following regularity, namely, with a decrease in the crystallinity and, accordingly, with an increase in the amorphicity degree of the sample, the amount of sorbed water increases proportionally (see e.g., Figure 6). This indicates that water molecules are captured by the polar groups in the amorphous domains of cellulose.

If at different relative vapor pressures, $\varphi = P/P_o$ from 0.1 to 0.9, the linear dependence $S = F(Y)$ is extrapolated to the S -values corresponding to $Y = 1$, then the general isotherm of WV absorption in amorphous domains (AD) of cellulose can be obtained (Figure 5). A similar general isotherm can be calculated also using the Gibbs-Duhem thermodynamics of binary systems [9] together with the Van Krevelen method for contributions of various functional groups of biopolymers to the sorption of water molecules [24].

This general isotherm can be presented in a linear form in coordinates $1/Sa = F(-\ln\varphi)$, as shown in Figure 7

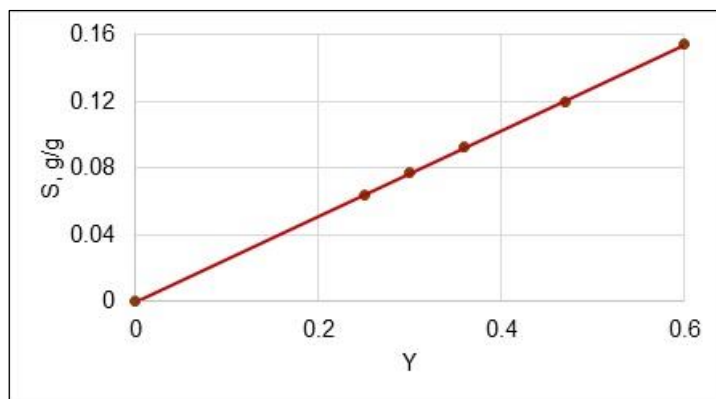


Figure 6 Dependence of sorption value (S) of samples on degree of amorphicity (Y) at P/Po=0.7

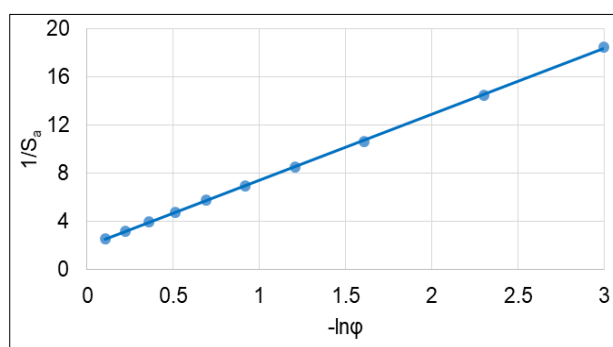


Figure 7 Linear form of general isotherm of WV absorption in AD of cellulose

The extrapolation of the linear plot $1/S_a = F(-\ln\phi)$ to $\ln\phi = 0$ gives the value $1/S_{0,a}$, from which the maximum sorption value, $S_{0,a} = 0.506$ g/g, was found. In addition, the slope coefficient (k) of the plot was determined and coefficient $C = kS_{0,a} = 2.7$ was calculated. As a result, the following simple equation of the isotherm was derived:

$$S_a = S_{0,a} / (1 - C \ln\phi) \dots \dots \dots (5)$$

To derive the isotherm equation for a semicrystalline sample having an amorphicity degree, Y, it is sufficient to introduce the Y-value in the eq. (5).

$$S = Y S_{0,a} / (1 - C \ln\phi) \dots \dots \dots (6)$$

An example of the isotherm calculated for a semicrystalline sample of MP (MP-C) having $Y = 0.47$ is shown in Figure 8. The experimental isotherm of this sample (MP-E) is also presented.

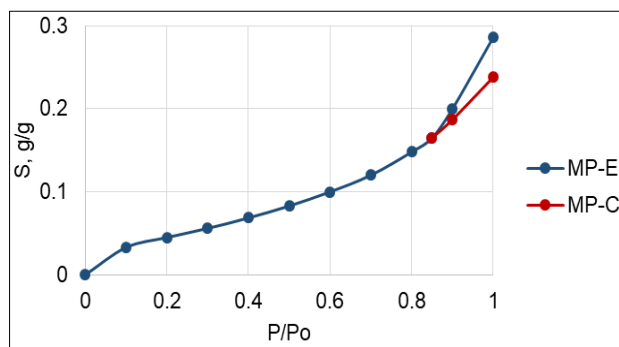


Figure 8 Calculated (MP-C) and experimental (MP-E) isotherms for MP sample

Comparison of the experimental and calculated isotherms for the MP sample showed that in the φ -range from 0 to 0.9, these isotherms are practically identical. However, at $\varphi=P/P_0 > 0.9$, a deviation of the calculated isotherm from the experimental one is observed. This phenomenon is caused by the known fact that at high relative vapor pressures, along with molecular sorption of water by polar groups of a low-porous hydrophilic biopolymer, also capillary condensation of WV occurs, which increases the amount of water in this polymer [2, 22, 23]. However, using calculations by the eq. (6), it is possible to separate the molecularly sorbed water from the capillary water as it is shown, for example, in Figure 8.

The studies have shown that the sorption value is directly proportional to the content of amorphous domains, Y , in cellulose samples. If $Y=1$, then the general isotherm of WV absorption in AD of cellulose can be obtained (Figures 5 and 9), which is described by the eq. (5). This isotherm consists of four specific sections, namely, I – initial steep stage, II – gradually increasing stage, III – rapidly increasing stage, and IV – final sharply rising stage.

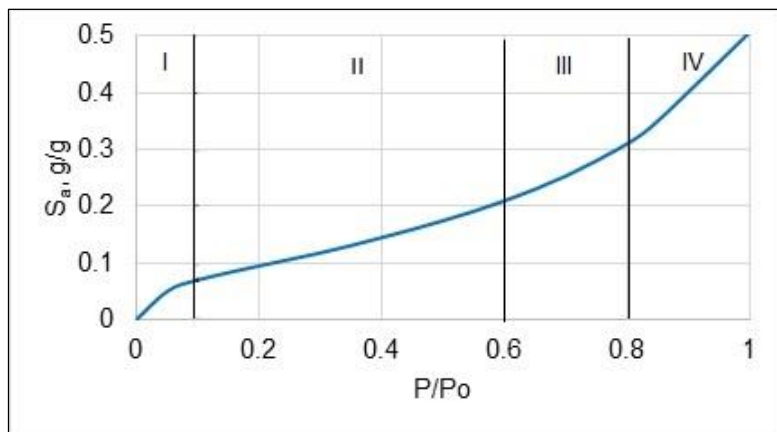


Figure 9 General isotherm of water vapor absorption in amorphous domains

The maximum amount of water absorbed by AD at $\varphi=1$ is $S_{o,a} = 0.506$ g/g or about 4.6 mol H₂O per mol of anhydroglucose unit (AGU) of cellulose. Considering that one AGU contains five polar groups, three hydroxyl, and two ether groups, it can be calculated that each polar group can attach less than one water molecule. Thus, monomolecular sorption of water molecules in AD of cellulose is achieved only at a maximum vapor pressure $\varphi=1$. This behavior distinguishes such polar biopolymer as cellulose from low- and non-polar polymers, in which water molecules cover the surface of pores with a monomolecular layer at a low vapor pressure. Since $S_{o,a}$ corresponds to monolayer capacity, the full specific surface area of AGU in amorphous domains of cellulose, calculated by eq. (2), will be $S_{sp,a} = 1800$ m²/g.

Thus, all obtained results prove that the sorption mechanism in the entire φ range is the absorption of water vapor by amorphous domains of semicrystalline cellulose materials. This model based on the absorption mechanism allows:

- Determine the degree of amorphicity (Y) and/or crystallinity (X) of the semicrystalline sample from the experimental sorption value (S), e.g., at $\varphi=0.7$,

$$Y = S/S_o; X = 1 - S/S_o \dots \dots \dots (7)$$

where

$$S_o = 0.26 \frac{g}{g} \text{ at } \varphi = 0.7$$

- Find the maximum amount of water absorbed by the semicrystalline sample at $\varphi=1$,

$$S_m = Y S_{o,a} \dots \dots \dots (8)$$

where

$$S_{o,a} = 0.506 \text{ g/g}$$

- Calculate the sorption isotherm for any semicrystalline cellulose sample according to eq. (6), knowing only one characteristic, the degree of amorphicity (Y) or crystallinity (X), since $Y=1-X$
- Separate the molecularly absorbed water from the capillary water by the difference between experimental and calculated by eq. (6) sorption values at $\varphi>0.9$; Note, the capillary water is freezing, which distinguishes it from non-freezing molecularly absorbed water [2, 19]
- Estimate the inflection point of the initial stage of the isotherm, so (g/g),

$$s_o = a Y \dots \dots \dots (9)$$

Where

$$a = 0.095 \text{ g/g}$$

- Estimate the nominal BET-specific surface area of the wet cellulose using eq. (10) or (11),

$$\text{Ssp (W)} = K Y \dots \dots \dots (10)$$

Or

$$\text{Ssp (W)} = A a Y \dots \dots \dots (11)$$

Where

$$K = 335 \text{ m}^2/\text{g}, \text{ and } A = 3516 \text{ m}^2/\text{g}$$

- Calculate the full specific surface area of the wet semicrystalline cellulose sample, as follows,

$$\text{Ssp, o (W)} = A S_{a, o} Y \dots \dots \dots (12)$$

Or

$$\text{Ssp, o (W)} = K_o Y \dots \dots \dots (13)$$

Where

$$K_o = 1800 \text{ m}^2/\text{g}$$

Discussing the absorption process of water vapor by cellulose materials, an additional problem arises associated with the glassy state of the main part of amorphous domains (AD) of this biopolymer at room temperature. As known, low-porous glassy polymers have a very small free volume, which hinders the penetration of molecules of various sorbates [24]. Therefore, also low-porous glassy hydrophilic polymer, such as cellulose, theoretically should be inaccessible for water molecules [12]. For this reason, one would expect that the sorption of water vapor by glassy amorphous domains of cellulose at the low and medium φ -values should be negligible, and begin only at elevated vapor pressure, when the glass transition temperature of humid amorphous domains decreases below the temperature of sorption experiment, 298 K. However, the experimental sorption isotherms do not support this hypothesis because even at the low φ -values the sorption of VW by AD of cellulose is quite noticeable, which requires an explanation.

Structural studies have shown that amorphous domains of cellulose have a heterogeneous packing since they consist of densely (DPC), medium (MPC), and loosely (LPC) packed clusters with different energies of hydrogen bonds [21]. The estimated density of DPC is 1.48, MPC is 1.44, and LPC is 1.35 g/cm³. In addition, it is known that the density of CI crystallites is 1.62 g/cm³ and their molar volume is 100 cm³/mol [25]. Using these data, free volume (V_f) in the packing of the clusters was calculated:

$$V_f = (V_{ac} - V_{cr})/N_A \dots \dots \dots (12)$$

Where V_{ac} and V_{cr} are molar volumes of amorphous cluster and crystallite, N_A is Avogadro number.

Table 2 Density (ρ_{ac}), molar (V_{ac}) and free (V_f) volumes of various clusters in AD

Cluster	$\rho_{ac}, \text{g/cm}^3$	$V_{ac}, \text{cm}^3/\text{моль}$	$V_f \text{ cm}^3/\text{AGU}$	V_f/V_w
DPC	1.48	109	1.50×10^{-23}	0.50
MPC	1.44	112	2.00×10^{-23}	0.67
LPC	1.35	120	3.32×10^{-23}	1.11

From Table 2, it follows that the glassy, densely (DPC), and medium (MPC) packed clusters are inaccessible for sorbate because their free volumes are less than the volume of the water molecule, $V_w = 2.99 \times 10^{-23} \text{ cm}^3$. On the other hand, in loosely packed clusters (LPC) local mobility of small segments is possible [21], which creates a free volume sufficient for the penetration of small water molecules.

As a result, at the initial steep absorption stage I (Figure 9), water molecules can penetrate in loosely packed clusters of AD and intensively sorb by polar groups of these clusters. This initial stage of absorption of VW by polar groups in LPC is accompanied by a high exothermic heat effect [2, 26]. The beginning sorption of water molecules in loosely packed clusters leads to a weakening of the hydrogen bonds in neighboring medium-packed clusters, which promotes further gradual sorption of water molecules at stage II. This process continues until the medium and densely packed clusters soften under the plasticizing effect of sorbed water, which leads to a rapidly increasing stage III (at $\varphi > 0.6$) and a final sharp rising stage IV (at $\varphi > 0.8$).

The final stage of the absorption process at $\varphi > 0.9$ can be complicated by capillary condensation in mesopores forming via relaxation of internal stresses after the complete softening of wet amorphous domains of cellulose [2].

4. Conclusion

The sorption of water vapor (WV) by various celluloses has been studied in this research. To describe sigmoidal sorption isotherms for cellulose materials, various models have been proposed. After critical analysis of known models, the improved absorption model was developed to explain the interaction of VW with cellulose. Since crystallites are inaccessible for water, water molecules can be trapped only by polar groups of non-crystalline (amorphous) domains of cellulose materials. The developed model permitted obtaining the general absorption isotherm of water molecules in amorphous domains of cellulose. Moreover, the equations were derived, which describe both the general isotherm and isotherm of any semicrystalline cellulose sample, when its crystallinity or amorphicity degree was pre-determined. Based on the absorption model, various characteristics can be found, e.g., degrees of amorphicity and crystallinity, the maximum amount of absorbed water, the specific surface area of wet cellulose, water, the amount of capillary condensed water, etc. The cluster structure of amorphous domains of cellulose and the contribution of various clusters to the absorption of water molecules were discussed.

Compliance with ethical standards

Disclosure of conflict of interest

The author of this paper hereby declares that there is no conflict of interest.

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